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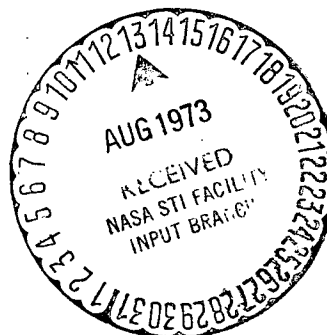
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EFFECT OF BOUNDARY SURFACE-ACTIVE VAPORS ON THE BEHAVIOR OF STEEL DURING SLIDING FRICTION[†]

By

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Report from the Governmental Materials Testing Institute
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The wearing down of steel Ck 45 to Ck 45 was measured at low   */183
sliding speeds on the Siebel-Kehl machine, in the presence of def-
inite vapor concentrations of cyclohexane, water, and acetone. With
increasing vapor concentration, wear increases continuously in a
steam atmosphere, while a maximum forms already at quite low con-
centrations, with cyclohexane and acetone. The difference in the
amount of wear is considerable. The environmental medium must be
held constant during wear experiments.

1. Introduction and Problem Definition

The wearing process is influenced by a large number of quanti-
ties, whose effects are partially unknown. They are already con-
tained in the so-called initial and final conditions (Figure 1).
Wear further occurs through materials changes and materials re-
actions with the surrounding medium. Besides the basic material,
the opposing material, the intermediary material, movement and load,

the interstitial medium -- decisive in lubrication -- also deter-
mines the wearing process. This medium can initiate tribophysical
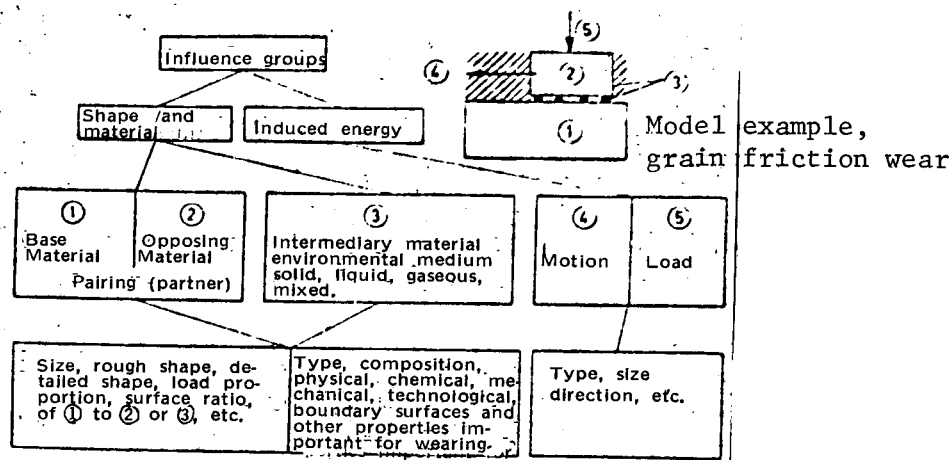and tribochemical reactions on the surface [1].

Figure 1. Groups and quantities of influence in the
wearing process. Analysis of initial conditions.

The surface energy of the solid material is reduced by ad-
sorbed layers. In addition, especially for unlubricated friction,
a limited separation of the two sliding partners, and a consequent
reduction of adhesive forces, is generated. For unlubricated
sliding in air, the differential adsorption power of oxygen and
steam can have decisive effects on wear and tear. This is apparent
from results of sliding friction experiments with the Siebel-Kehl
wear test machine, in the range of "heavy wear" of the pairing
soft iron/soft iron (Figure 2). The weight loss occurring over
the running path is shown as determined by weighing after various
intervals. The sliding speed was deliberately kept low, at
v = 0.05 m/s, in order to keep sample heating within narrow tolerances,
and thus to allow the influence of humidity to have its effect.

2

Figure 2. Results of sliding friction experiments with
the Siebel-Kehl machine on soft iron/soft iron, for
determining the influence of humidity in the air.

At low humidity (about 2%), an oxidation layer results from the   /184
wearing process and consists predominantly of Fe_2O_3. This keeps
abrasion low, since this occurs according to the mechanism of
action layer wear. With increasing humidity, wear increases, more
rapidly at lower ranges, as a result of the declining proportion of
formed oxygen layers, until finally in humid air a value is reached
which is almost 200 times as large as that reached in dry air [2].
At high humidity, a peculiarity appears. After uncertain running
path, usually depending on the particulars of the sample, the curve
has a kink, which is also indicated by a drop in the friction mo-
ment; further rise remains flat, smaller than for dry air. The
reason is the formation of oxydic support points, which probably

3

consist of Fe_3O_4.

According to the experimental results of Weissmantel [3] and Ertl [4] concerning the adsorptive power of steam and oxygen, steam first replaces oxygen from the adsorption layer, in consequence of its boundary surface activity, and consequently inhibits oxidation of the surface. In the long run, oxygen uptake is accelerated in a long-term reaction. But in the sliding process, it is a question of a locally occurring alternating short-term influence on adsorption and desorption, and of the generation of new surfaces in the microdomain. Consequently, a displacement of oxygen by steam is effected, and adsorption of water molecules first leads to protection of the surface against oxygen adsorption. If the experiment is interrupted, and consequently also the continuous alternating influence, then, on the long term, oxygen uptake is accelerated in the form of a long-term reaction. Possibly this temporally different sorption mechanism offers an interpretation for the observed reversal of the wear mechanism.
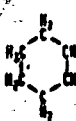
Environmental medium	Structural formula	Molecular weight	Gas constant m·p E_0 °C	Vapor pressure (20°C) Torr	Surface tension $\delta_{fh/cm}$	Dipole moment D·byn	Polarity $E_f(i)$ °C, kcal/Mol
Cyclohexane		84,2	100	77	25,0	0 0,2	
Water	H,0	18,0	47,0	17,5	72,8	1,84	63,1
Acetone	CH_3-C-CH_3	58,1	14,6	185	23,7	2,95	42,2

Figure 3. Collation of various boundary surface active media. In particular, cyclohexane, water, and acetone were used.
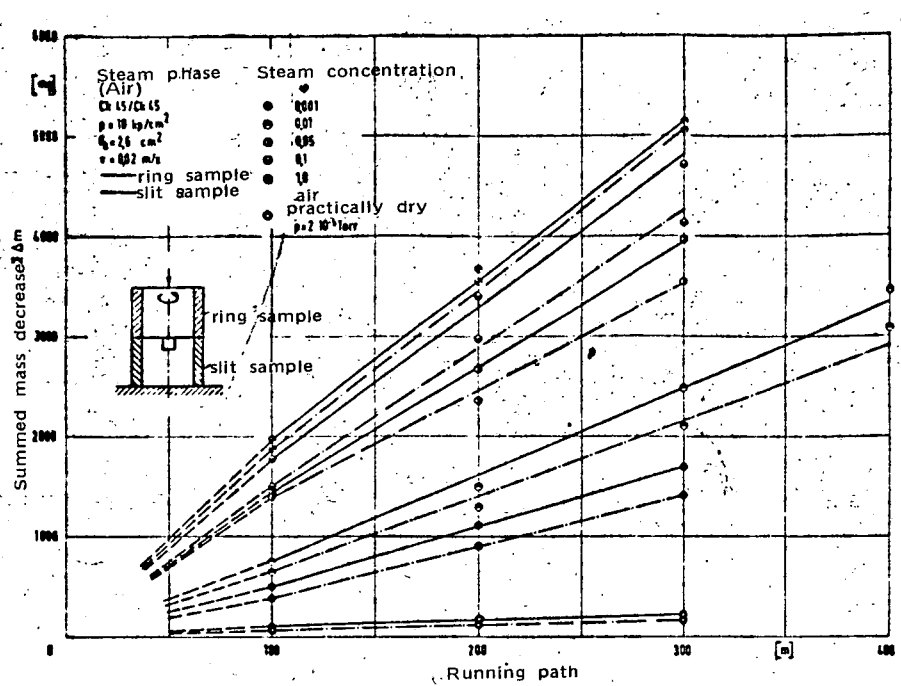
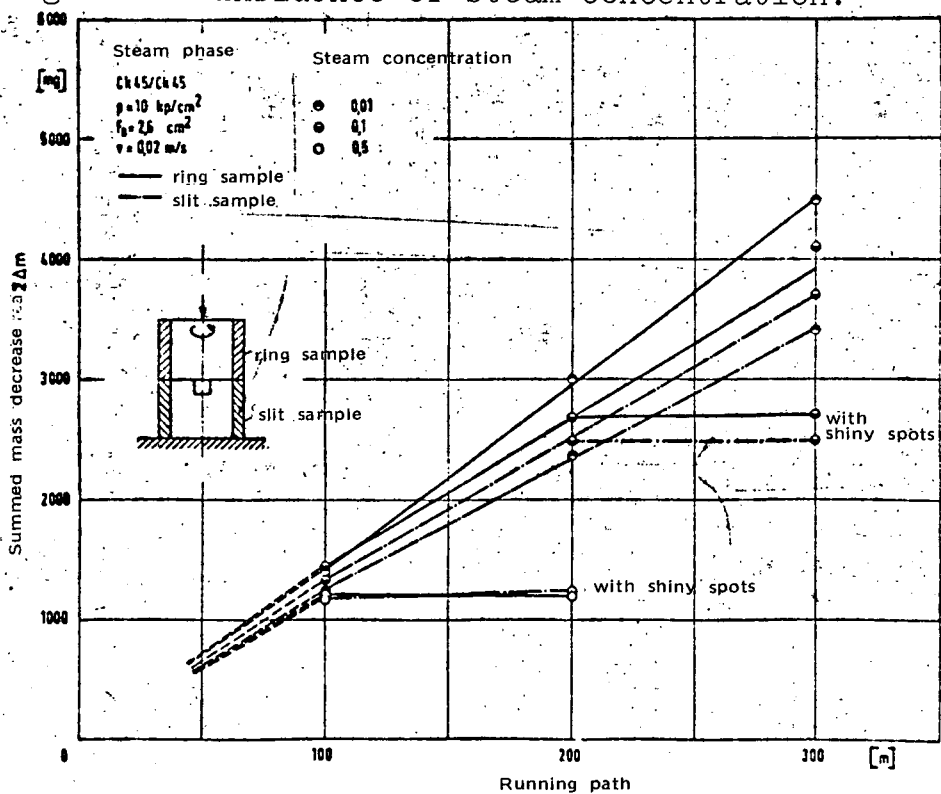Figure 4. Influence of steam concentration.

Figure 5. Influence of concentration of acetone vapor.

Materials which oxidize either little or not at all, because of their slower chemical reaction rates, show a markedly smaller increase of wear through increased humidity. For Ms 58/steel C 45 the increase is only about twofold. Probably a corrosive component plays a role; possibly the effect is based on the rehbinder effect, according to which boundary surface active materials, such as steam, produce a weakening of the surface and a diminution of plasticity [5]. The behavior of mineral materials, when they are split into particles, is also supposed to be influenced by this effect [6].

These effects must come to the fore particularly in wear and tear under use, since a new surface always is generated as a result of material ablation. This new surface is particularly reactive and favors tribophysical and tribochemical reactions. Besides adsorption of the surrounding medium, chemisorption [4], and sometimes chemical splitting of the adsorbed molecule can occur, initiated by the high energy concentration at contract sites [7,8]. This can considerably influence the wear process.

Wear can be regarded as an energy transformation process, where predominantly mechanical energy is converted mainly into work of deformation and separation. The separation work finally appears as surface energy of the free abrasion particles. Wear increases all the more, the smaller is the surface energy of a material. This energy is lowered through the surrounding medium, as a consequence of adsorptive deposition. Since the forces operative in adsorption are electrostatic, it can be assumed that media with different electrostatic dipole moments (dimension of the measuring unit 1 Debye = 10^{28} Cb·cm) produce different wear effects. Possibly the polarity [9] has an effect also.

2.   Materials, Surrounding Media, Experimental Conditions and Execution

To investigate the effect of various boundary surface active vapors in unlubricated friction, experiments were performed with a vacuum wear test installation. In this installation, the frontal /185 surfaces of the 2 cylindrical sample groups of the type similar pairing Ck 45 slide on one another [2], according to the principle Siebel-Kehl. The sliding surfaces run against one another, where the size of the surface of the upper ring sample is 3 cm^2, and that of the lower one is 2.6 cm^2. The lower probe, which, in contrast to the upper probe, does not rotate, is situated in such a way that the turning moment generated by friction can be measured. The measurement of the friction force is made with an inductive force measuring probe over a carrier frequency measurement amplifier and a compensation line writer.

The intermediate materials chosen differ primarily in their dipole moments,* see Figure 3.

For the experiments, vapors of cyclohexane, water, and acetone, at various concentrations, were admitted into the vacuum apparatus, at a pressure of $2 \cdot 10^{-5}$. The media used are arranged according to dipole moments. Cyclohexane almost zero, water 1.85, and acetone 2.95.

For a further subsequent test, the polarity of the solvent medium is given. It is determined by the effect of the solvent on a standard process depending on the solvent (speed of a chemical reaction, light absorption of a solvatochromatic dye). In this way, it is possible to derive empirical parameters of solvent polarity, from the rate constants which are known for many solvents, or from their absorption maxima. The E_t values calculated from a particular model for pyridinium-N-phenolbetain are able to characterize the

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* Taken for the gas phase (10).

polarity of solvents, because of the unusually great displacement of the solvatochromic bands [9].

3. Experimental Results

Figure 4 shows the summed mass decrease over the running path, for air at $2 \cdot 10^{-5}$ Torr, as well as for various concentrations of steam ϕ^2 = 0.001, 0.01, 0.05, 0.1, 1.0. Ring and slit samples differ only slightly in the extent of wear. Consequently, the average value of both wear curves can be utilized for further evaluation. After the initial period of the first interval, the experimental points, from 100 m of running path, follow approximately a straight line. This means that the wear, relative to the running path, remains nearly constant under the prevailing conditions. This fact is the basis for further evaluation. The inclination of the straight line increases with increasing steam concentration.

$\eta = P_k/P_d$ with

P_k = vapor and

P_d = saturation vapor pressure

In vacuum (10^{-5} Torr) the friction number is in the neighborhood of 1, in consequence of the adhesive forces which are quite effective here for the relatively pure metal surface. For small traces of steam it already falls to about 0.7 to 0.8, and remains nearly constant over the entire concentration range.

In a cyclohexane atmosphere, a linear course likewise results for all concentrations, but the inclination of the straight line does not increase with concentration, but, after the maximum value at ϕ = 0.01, declines again. For acetone, Figure 5, the linear course occurs only for low vapor concentrations of ϕ = 0.01. For ϕ = 0.1, a decrease of the relative wear occurs to a fraction of the previous value. The slide surfaces show shiny spots. Already during the course of the experiment, a sudden decrease in the friction number occurs from 0.6 to 0.2. This leads to the conclusion that

8

a change occurs in the wear mechanism. This transition occurs directly at the beginning of the new running path interval. If the experiment is not interrupted, then no transition occurs to the shiny spot wear. For $\phi = 0.5$, shiny spots occur - likewise connected with low wear and low friction, always at the beginning of the second running path interval, that is directly after the initial period. Here too, no transition occurs during the running course. These results indicate the type of wear testing.

Texture investigations were performed on one wear sample each, with and without shiny spots, on 11° diagonal sections, Figure 6. The two running surfaces differ in their surface geometry. The samples without shiny spots have a profile with relatively "tipped" cones. Because of the diagonal cut, these are additionally peaked. The sample with shiny spots, on the other hand, has more plateaus, which indicate favorable support behavior. The texture in the surface domain, even at large magnification, as well as the micro-hardness, show no detectable differences. But the microprobe, however, determined an oxygen concentration (about 50%) and a carbon dioxide concentration (25%) in the neighborhood of the shiny spots, while these elements could not be demonstrated in the same measuring range, for the sample without shiny spots.

For further evaluation, the wear values v_s, relative to the running path are shown (in mm/km) over a range of vapor concentra- /186 tions (Figure 7). Starting with the vacuum value (air) of $2 \cdot 10^{-5}$ Torr, two basically different courses result. For a steam atmosphere, wear increases continuously with increasing concentration, while for the hydrocarbons cyclohexane and acetone, a maximum occurs for the wear at fairly low concentrations.

The representation over the range of vapor concentration is not quite correct, however, for comparative judgement, since the partial pressures of such vapors behave like the corresponding

9
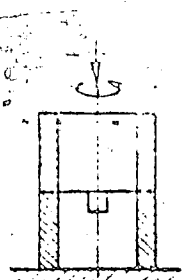
high vacuum wear
    station
C 45/C 45

surface of the slit
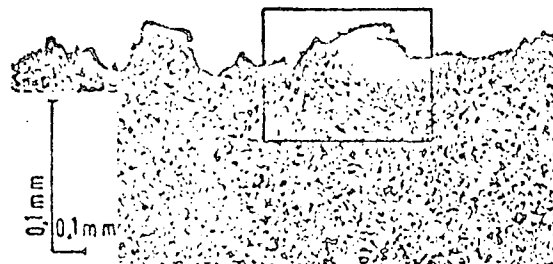   sample
$A_s = 2.6 \text{ cm}^2$

normal force
$F_N = 26$ kp

slide speed
v = 0.02 m/s

acetone atmosphere
$\phi = 0.5$

WITHOUT SHINY SPOTS

0.1 mm

WITH SHINY SPOTS

0.1 mm

25 µm

25 µm

Figure 6. Formation of slide surface with and without
shiny spots, diagonal section inclined 11 degrees to the
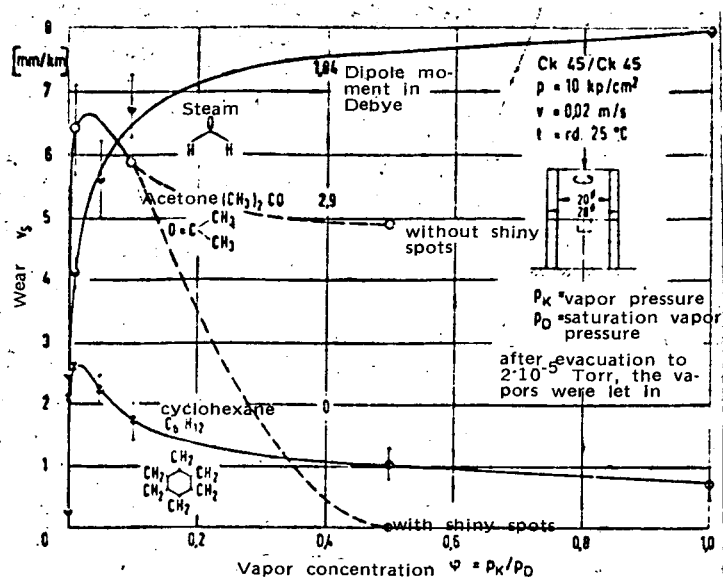running path.

Figure 7. Juxtaposition of wear values determined in water-, acetone-, and cyclohexane-vapor as a function of concentration.

vapor pressures at constant ϕ. But the decisive factors are the amount or the number of molecules present, which are proportional to the chamber pressure P_k, if constant vapor temperature is assumed. For this reason, Figure 8 shows the wear relative to the chamber pressure.
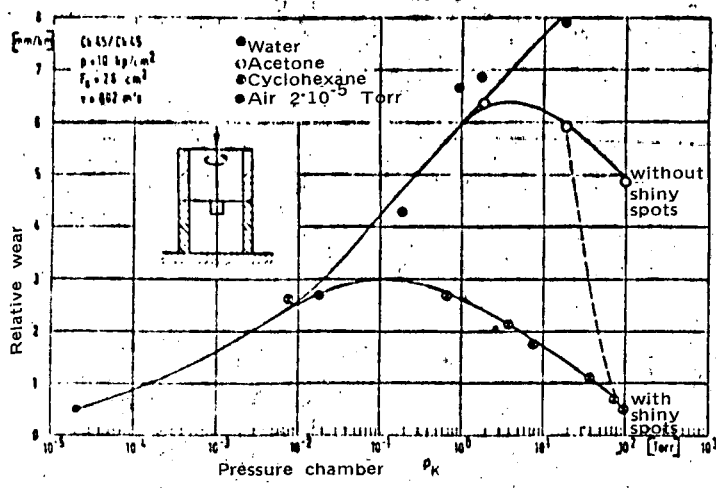

Figure 8. Juxtaposition of the results shown in Figure 7, as a function of chamber pressure.

11

Compared to the representation of Figure 7, it can be seen that the maxima for hydrocarbons lie at different vapor pressures. With decreasing partial pressure, the number of vapor molecules becomes smaller, and the environmental condition in the chamber becomes more and more similar to that of vacuum. For this reason, the wear curves were made to pass through the experimental point $2 \cdot 10^{-5}$ Torr (air). The cyclohexane and acetone curves first rise, then fall after the maximum value is reached. Possibly, this decrease of wear is connected with a lubricating effect resulting from molecules adsorbed on the slide surface; some evidence for this comes from the friction number, which, for acetone, lies lower, at a value of 0.6, then for water, with $\mu = 0.7$ to 0.75. For steam, no decrease appears with increasing pressure, as could already be seen from Figure 7. For cyclohexane and acetone, it is true that increasing wear appears for increase in dipole moment. But water, with a dipole moment between cyclohexane and acetone, does not fit this pattern. By contrast, the empirical value of the polarity E_t [9] appears to reproduce correctly the order of wear for water and acetone. No E_t values were available for cyclohexane. But it can be assumed that it is lower that that of acetone. Possibly, the number of carbon atoms in the compound plays a role relative to the wear behavior. A dissolution of the chemical bond in consequence of the high energy concentration at the contact sites has already been demonstrated for several friction processes [7,8]. In the decomposition of hydrocarbons, the resulting carbon can act as a lubricant, and can consequently inhibit wear. This further increases the lubricating effect, which is already caused by adsorption of vapor molecules. This effect is stronger for cyclohexane, with 6 carbon atoms per molecule, than for acetone, with 3 carbon atoms. Similarly, wear increases as the number of carbon atoms decreases.

12

For acetone, further tribochemical effects play a role in the region of the shiny spots. These affect a transition into a kind of wear minimum.

An unambiguous dependence of the size of abrasion particles on the vapor concentration could not be observed with the used /187 method of determination. But differences did appear when different vapors were used. In paths using steam, the abrasion particles, regarded as a whole, are larger (40 to 1600 μm average diameter) than for cyclohexane (0.5 to 20 μm) and acetone (4 to 20 μm).

For the same amount of abrasion material, the newly generated surface is larger in proportion that the particles are smaller (surface proportional to the square of the diameter). Consequently, the hydrocarbons use more energy in the form of separation work than steam. Besides the decrease in surface energy, a shift of the distribution of deformation and separation energy occurs more towards the end. This leads to a suspicion of an embrittlement in the surface face domain which depends on material and on exposure.

4. Summary

The experiments, despite all difficulties in interpretation, show that different vapors have a considerable influence on the use behavior of steel Ck 45/Ck 45. It can be assumed that for milder requirements even clearer differences would have resulted. The boundary surface activity or the dipole moment appeared to play only a limited role, the polarity and the number of carbon atoms, on the other hand, seemed to be significant.

The experiments show how important it is to determine the surrounding medium during wear and friction experiments, and to hold it constant. An example is the water vapor content. They further indicate that the surrounding medium cannot be left out of consideration in the analysis of practical wear instances. A further important determination is that the wear process can be completely

13

overwhelmed by tribochemical effects, which effect a material change at the boundary surface.

At this place, we thank the German Research Society, Bad Godes- berg, for its financial support.

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